Equilibrium dec 7
Wednesday, December 7, 2022 5:12 PM

EQUILIBRIUM

Reversible Rx^n → which proceed in forward as well as in Backward direction.

⊛ Rate of Reaction for any Direction = Change in conc. of any species per unit time.
⇓
speed of Rx^n

Features of Equilibrium state of Rx^n

① only possible in Reversible Rx^ns.

② In Rev Rx^n, at Eq^m,

$$\boxed{\text{Rate of forward direction} = \text{Rate of Backward direction}}$$

③ for Rev Rx^n → Container must be closed.

④ Eq^m is Dynamic in Nature.

⑤ When Eq^m is achieved,
All measurable parameters (conc, T, P, V, moles, density, color etc.) becomes const for each species present in Rx^n.
⊛ $\boxed{\text{Change in conc. for any species at Eq}^m = 0}$

⑥ Catalyst equally increase rate of forward and Backward direction so that Eq^m is achieved faster without changing the Eq^m point and eq^m const (keq) & ΔH_{Rx} & ΔG_{Rx} & ΔS_{Rx}.

⑦ Eq^m of Rx^n can be achieved from either direction (forward as well as backward).

Equilibrium
→ $R_f = R_b$

Law of chemical Eq^m

k_f → Rate Const for forward dir^n
k_b → " " " Backward dir^n

$$aA(g) + bB(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} cC(g) + dD(g)$$

Gases → ideal
aqueous species → Sol^n is very dilute

R_f (Rate of forward dir^n) $\propto [A]^a[B]^b$

$$R_f = k_f[A]^a[B]^b$$

similarly, $R_b = k_b[C]^c[D]^d$

$PV = nRT$
$P = \left(\frac{n}{V}\right)RT$
$P = (C)RT$ → Conc. of Gas (Molarity)

At Eq^m, $R_f = R_b$

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

$$(K_c) = (K_{eq}) = \frac{k_f}{k_b} = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$

K_{eq} → Eq^m Const
K_c → When Conc (Molarities) are Considered.

$K_{eq} \to (K_c)$
$K_{eq} \to (K_p)$ ⇒ when Partial pressure of Gases are taken at Eq^m.

$$K_p = \frac{(P_C)^c_{eq}(P_D)^d_{eq}}{(P_A)^a_{eq}(P_B)^b_{eq}}$$

$P_C = \chi_C (P_{Total})$ → Eq^m pressure or Total Pressure at Eq^m
$P_A = \chi_A P_T$
$P_B = \chi_B P_T$
$P_D = \chi_D P_T$

eg: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_p = (P_{CO_2}) = \frac{n_{CO_2} \times RT}{V}$ → $(P_T = P_{CO_2})$

$K_c = [CO_2] = \frac{P}{RT}$

⊛ [Pure Solid | Liq] = const → taken as 1
⇓
Conc.

⊛ $P = cRT$
$P_A = [A]RT$
$P_T = P_{CO_2} = [CO_2]RT$

$$[CO_2] = \frac{P}{RT}$$

eg: $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$

$$K_c = \frac{[CO_2]_{eq}}{[O_2]^2_{eq}[CH_4]_{eq}}$$

$$K_p = \frac{(P_{CO_2})}{(P_{O_2})^2(P_{CH_4})}$$

Relat^n b/w Kp and Kc

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \qquad P_A = [A]RT$$

$$= \frac{[C]^c[D]^d (RT)^{c+d}}{[A]^a[B]^b (RT)^{a+b}}$$

$$= K_c \cdot (RT)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_c \cdot (RT)^{\Delta n_g}}$$

Δn_g → Diff of Stoich. Coeff for gaseous species

eg: $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$
$K_p = K_c(RT)^{\Delta n_g}$
$K_p = K_c \cdot (RT)^2$

Note: $R = 0.0821$ L-atm mol^{-1} K^{-1}
$\approx 1/12$
$RT \Rightarrow \frac{T}{12}$

(iii) $T \approx 12K$
$\frac{T}{12} = 1$
$(1)^{\Delta n_g} = 1$
Δn_g can be 0, -ve, +ve
$\boxed{K_p = K_c}$

(i) $T > 12K$
$\frac{T}{12} > 1$
$\left(\frac{T}{12}\right)^{\Delta n_g} > 1$; $\Delta n_g > 0$ → $K_p > K_c$
$\left(\frac{T}{12}\right)^{\Delta n_g} < 1$; $\Delta n_g < 0$ → $K_c > K_p$

(ii) $T < 12K$
$\frac{T}{12} < 1$
$\left(\frac{T}{12}\right)^{\Delta n_g} > 1$; $\Delta n_g < 0$ → $K_c < K_p$
$\left(\frac{T}{12}\right)^{\Delta n_g} < 1$; $\Delta n_g > 0$ → $K_c > K_p$

eg: (i) $CH_3COOH(aq) + NaOH(aq) \rightleftharpoons CH_3COONa(aq) + H_2O(l)$ } example of Heterogeneous Eq^m.

$$K_c = \frac{[CH_3COONa]}{[CH_3COOH][NaOH]}$$

(ii) $CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$ } Example of Homogeneous Eq^m.

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]}$$

$H_2O(l) \rightleftharpoons \boxed{H_2O(\text{vapour})}$
$K_p = P_{H_2O}(v) = $ V.P of H_2O
→ V.P is Eq^m Const.

Factors affecting Eq^m Const (Keq)

① Temp
② Mode of Representation of Rx^n
→ Representat^n of Rx^n Changes, Rx^n becomes new & Every new Rx^n has new Eq^m Const.

① Temp

$\boxed{K_{eq} \propto T}$; ΔH = +ve (Endo)
T↑, Keq↑
T↓, Keq↓

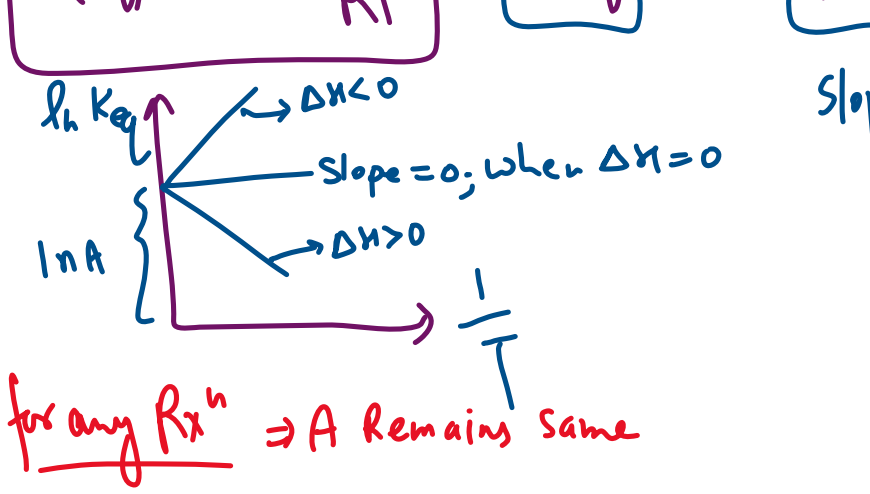
$\boxed{K_{eq} \propto \frac{1}{T}}$; ΔH = -ve (Exo)
T↓, Keq↑
T↑, Keq↓

→ Rel^n b/w T & Keq
Van't Hoffs Eq^n

i) $\boxed{K_{eq} = A e^{-\frac{\Delta H}{RT}}}$ A → Const (pre-exponential)

(ii) $\boxed{\ln(K_{eq}) = \ln A - \frac{\Delta H}{RT}}$ ⇒ $\underset{y}{\boxed{\ln K_{eq}}} = \underset{c}{\boxed{\ln A}} + \underset{m}{\boxed{\left(-\frac{\Delta H}{R}\right)}}\underset{x}{\boxed{\frac{1}{T}}}$

Slope $= -\frac{\Delta H}{R}$



(iii) for any Rx^n ⇒ A Remains same
at $T_1 \to K_{eq} = k_1$
at $T_2 \Rightarrow K_{eq} = k_2$

$$\boxed{\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

$$\boxed{\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$

② Mode of Representat^n

(i) Reversal of Rx^n:-
eg $A \rightleftharpoons B$; $K_{eq} = K_1 = \frac{[B]}{[A]}$
$B \rightleftharpoons A$; $K_{eq} = \frac{[A]}{[B]} = K_2$
$K_2 = \frac{1}{K_1}$

(ii) Change in Stoichiometric coeff
$A \rightleftharpoons 2B$ $K_1 = \frac{B^2}{A}$
$3A \rightleftharpoons 6B$ $K_2 = \frac{B^6}{A^3} = K_1^3$

(iii) Addition of Rx^n :- Eq^m const will multiply.
eg $A \rightleftharpoons 2B$; $K_1 = [B]^2/[A]$
$2C \rightleftharpoons E$; $K_2 = \frac{[E]}{[C]^2}$
$A + 2C \rightleftharpoons 2B + E$; $K_{eq} = \frac{[B]^2[E]}{[A][C]^2} = K_1 \times K_2$

Q $\frac{1}{2}B \rightleftharpoons \frac{1}{4}A$; Keq in terms of K_1?
$\frac{1}{(K_1)^{1/4}} = K_{eq}$

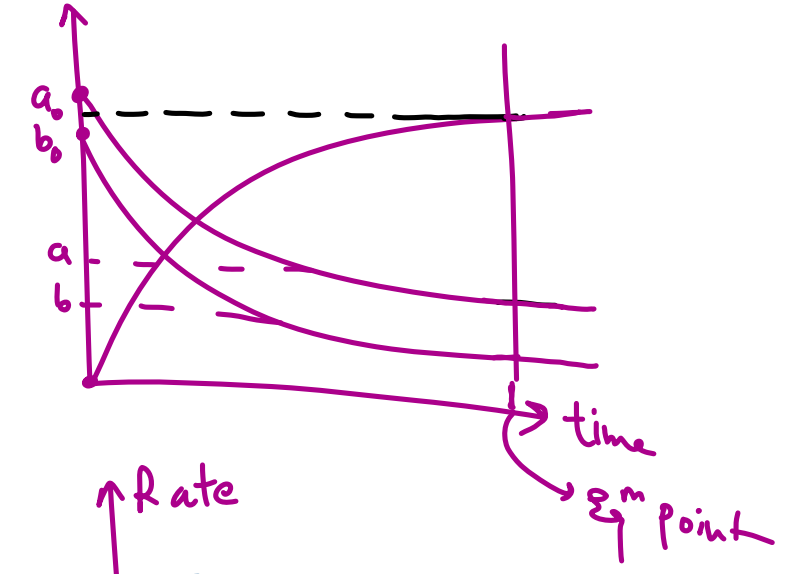
eg
$A \rightleftharpoons B$ K_1
$C \rightleftharpoons D$ K_2
$A - C \rightleftharpoons B - D$
or
$A + D \rightleftharpoons B + C$ $K_{eq} = \frac{K_1}{K_2}$

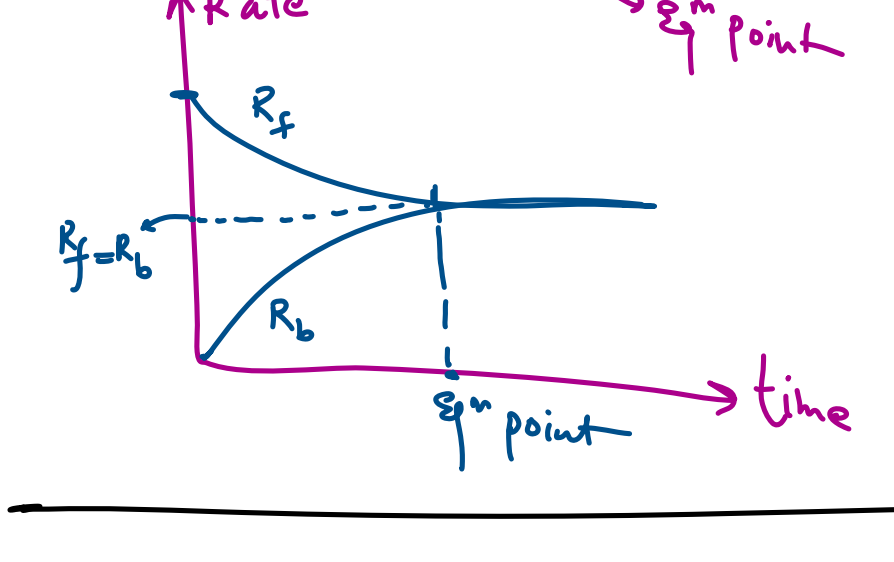
Solve Q→73 (Pg-123) Q→61 (Pg-122)
Q→96 (Pg-126)
Q→91
→ $\frac{1}{K_1^2} : K_2$

Initially
$1A + 1B \rightleftharpoons 1C$
t=0: a_0 b_0 0
t=t at Eq^m: $(a_0 - x)$ $(b_0 - x)$ (x) → a, b, c

$R_f = k_f[A][B]$
$R_b = k_b[C]$

$(R_f = R_b)$ ⇒ $[A]_{eq} = a_0 - x$
$[B]_{eq} = b_0 - x$
$[C]_{eq} = x$





Q: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Initially 3 moles of N_2 & 4 moles of H_2 are added in 2L Container at 300K. If at Eq^m 1 mole of NH_3 is formed. Find K_c of Rx^n.

Sol^n:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
t=0: 3 mole, 4 mole, 0
at Eq^m: $3 - x$, $4 - 3x$, $\boxed{2x}$
$3 - \frac{1}{2}$, $4 - \frac{3}{2}$, 1
$\left(\frac{5}{2}\right)$

Given moles of NH_3 at Eq^m = 1 = 2x
$(x = \frac{1}{2})$

Conc at Eq^m $[N_2]_{eq} = \frac{5/2}{2} = \frac{5}{4}$ mol/L
$[H_2]_{eq} = \frac{5/2}{2} = \frac{5}{4}$ mol/L
$[NH_3]_{eq} = \frac{1}{2} = \frac{1}{2}$ mol/L

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(1/2)^2}{(5/4)(5/4)^3}$$

$\boxed{K_p, K_c \Rightarrow \text{Unitless}}$

Concept of Le-Chatlier's Principle

"It states that if an external stress is applied to a system in Eq^m, the Eq^m for the time being gets disturbed. As a result system moves in a direction which tends to relieve the external stress and finally a new Eq^m is attained."

or

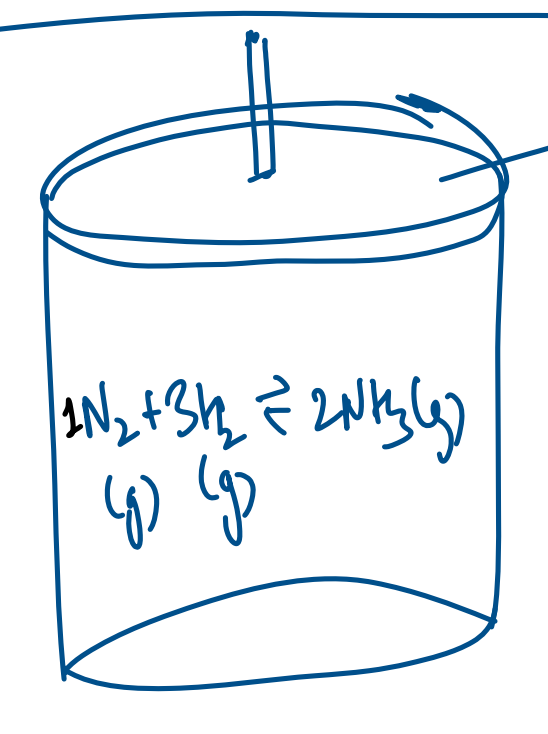
If Rx^n's Eq^m is disturbed by external stress (by changing T, P, V, Conc, or add^n of inert Gas); then Rx^n shift either forward or Backward dir^n to achieve new Eq^m.

(I) Effect of Change in conc. of gaseous or aqueous species

Reactant ↑es, Forward Shift
Product ↑es, Back "

Reactant Removed, Back "
Product " ; Forward Shift

(II) Effect of Pressure & Volume



Piston is pressed downward, Collision in Reactant side is increased more than in Product side; So Rx^n takes place to achieve Eq^m in Forward side.

⊛ P↑ (V↓); Eq^m shifts towards less no. of Gaseous molecule side.
P↓ (V↑es); " " " More " " " " "

(III) Temp Effect → only factor to change Eq^m const & Eq^m point.

$A + B \rightleftharpoons C$; ΔH = -x
or
$\boxed{\text{Exo } A + B \rightleftharpoons C + \Delta H}$

$C + E \rightleftharpoons F + H$; ΔH = +y
or
$\boxed{C + E + \Delta H \rightleftharpoons F + H}$ → Endo

T ↑es ; Run away from ΔH Side
T↓es, Run towards ΔH side

Q: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\boxed{\Delta H = -46.3 \text{ KJ/mole}}$

(T low) or high to favour the Rx^n. ?

Q: $2SO_3(g) \rightleftharpoons 2SO_2 + O_2(g)$; ΔH = +50
To Favour the Rx^n
i) T high ✓ or low
ii) P High or low ✓
(iii) Conc. of SO_2 ↑ or ↓ ✓

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
Q P ↑ or ↓ to favour Rx^n
No Effect of Pressure.

(IV) Add^n of inert gas (Ne, Ar, Kr, Sometimes N_2 etc.)

i) at const Volume, No effect of add^n on Eq^m point
ii) at const Pressure, Eq^m point shift towards more no. of gaseous moles.